

NATURAL VIBRATIONS AS CAUSE OF ENERGY FLUCTUATIONS
AND CHEMICAL CONVERSIONS

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NATURAL VIBRATIONS AS CAUSE OF ENERGY FLUCTUATIONS
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The mechanism of monomolecular reactions, including dissociation and transformation, of larger molecules is explained on the basis of intramolecular energy fluctuations in elastic waves, initiating the reaction at the instant at which the amplitude, at a definite bond of the system, accidentally rises above a critical value due to interference of the waves. The fluctuation in energy of a given atom during a given time and the frequency with which the energy increases to an amount larger than kT (velocity constant times temperature) are calculated, substantiating the empirical finding that the temperature-independent factor of the velocity constant of monomolecular reactions has an order of magnitude of 10^{14} . In a system with a weak bond (colliding molecules, molecules striking the wall) the energy transfer is less than in a system with a stable bond. The frequency of a chemical reaction or other transformation due to exceeding a critical elongation of a certain atom or to lifting the atom to a higher energy level is calculated.

Summary

According to established experience, the velocity constant of monomolecular reactions in solutions and - as demonstrated recently - also in gases contains not only an exponential factor but also a quantity which always is of approximately the same order of magnitude, namely, 10^{14} . To explain this, we imagine that the energy in the molecule fluctuates in elastic waves and that the transformation takes place at the instant at which the amplitude at a certain bond, due to interference of the waves, accidentally is increased beyond a critical

amount. For the velocity constant, this yields a value of $\nu e^{-\frac{Q}{RT}}$, where ν denotes the frequency of the atomic vibration, i.e., has the correct order of magnitude.

1. Problem Formulation

Our investigations had the purpose of establishing a concept on the mecha-

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** Numbers given in the margin indicate pagination in the original foreign text.

nism of monomolecular reactions (dissociation and transformation) of larger molecules. Monomolecular gas reactions have frequently been discussed in recent times, but the papers (which will be mentioned later in the text) do not consider the mechanism of intramolecular processes and, for their characterization, use instead a constant that cannot be correlated with any other phenomenon. Our formulation was to make an interpretation of this constant possible. The concept is based on the assumption that the system consists of a number of atoms linked to equilibrium positions by quasi-elastic forces. The possible motions of such systems can be composed of natural vibrations which, by interference (beat), may produce considerable amplitudes at individual sites. For example, if we have four atoms arranged along a straight line, the system will have three natural vibrations. If only one of these vibrations is excited, then the amplitude of all atoms will be time-invariant and of the same order of magnitude. /440 Conversely, if - for example - all three natural vibrations are excited, the resultant beats will cause each individual bond to periodically absorb the major portion of the vibration energy. During this process, a transformation might occur in that a configuration is produced which, on dissipation of the energy, does not always return to the initial state* but, with approximately equal probability, changes to a new equilibrium position. In the same manner, a dissociation may take place as soon as the critical elongation attains the range of molecular forces. In accordance with the above concept, the discussion excludes per se the formation and degradation of diatomic molecules in the gas volume. This particular process formed the subject of one of our earlier papers (Ref.1). The process was correlated there with the Auger process. After K.F.Bonhoeffer and L.Farkas (Ref.2) had proved that the photochemical NH_3 dissociation represents a process similar to the Auger process, this problem was treated by R. de L.Kronig (Ref.3) on the basis of the new quantum mechanics and defined as a typically quantum-mechanical effect. The velocity of processes, produced by this effect, is much lower than that of the reactions considered here.

A neglect in this respect is constituted by the assumption of quasi-elastic bonds, which eliminates the scattering of the elastic waves and thus the superposition of ordinary heat conduction (Ref.4). In addition, the validity of our derivation, as stipulated, is restricted to transformations not connected with any electron jump.

A further restriction is produced by the use of classical instead of quantum-mechanical concepts. However, since only states with high quantum /441 numbers are involved here, even a stricter treatment on the basis of quantum

* Until now, it was conventional to subdivide the reaction process into two portions: "activation" and "transformation". "Activation" was assumed to proceed at an arbitrary velocity by intramolecular energy transfer while "transformation" was to take place spontaneously in accordance with a certain lifetime of the activated state, substantially influencing the reaction velocity. We reject this particular concept since, because of the reversibility of the elementary processes, the process that represents an "activation" for one direction of the reaction will be a "transformation" for the opposite reaction (our own concept corresponds to this stipulation).

mechanics will yield no different result*. Nevertheless, quantum mechanics is responsible for the fact that transformations which, according to conventional concepts, seem probable actually are not possible since, in addition to the classical integrals, further integrals of the equations of motion exist which reduce the probability of certain transitions (for example, from a singlet to a triplet state) to a very low value [according to Wigner (Ref.6) who is studying this aspect of the problem, as reported by F.London].

In addition to the reaction mechanism described here, quantum mechanics offers an entirely different explanation for the transformation process. It is possible that a nonmechanical skip of the energy barrier, separating the two modifications, takes place similar to that observed in radioactive processes (Ref.7). However, such a process would have a few peculiar characteristics of which it does not seem too probable that they could be applied to the known reactions. Specifically, the reaction velocity at absolute zero would still have a finite value and would not increase with the temperature in accordance with

$Ae^{-\frac{Q}{RT}}$, but much more slowly.

2. Energy Fluctuations within a Firmly Bound System

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Let us imagine an aggregate of atoms consisting of n atoms of essentially equal weight and held together by approximately equally strong forces. Let the most rapid natural vibration have the period $\frac{1}{\nu}$ and let the total energy of the system be E . The problem is to define the average time until, at a singled-out

* In the case of quasi-elastic bonds - in agreement with a paper by Schrödinger (Ref.5) - the transition to high quantum numbers can also be done individually.

Classically, the motion can be conceived as a superposition of natural vibrations. If the coordinates of the individual particles are replaced by "normal coordinates", i.e., coordinates that remain constant at all natural vibrations except one but execute a purely sinusoidal motion at this latter vibration, then the image point of the system in the configuration space moves in accordance with the equation

$$q_k = a_k \sin(\omega_k + \varphi_k) t \quad (\alpha)$$

From a quantum-mechanical viewpoint, an introduction of normal coordinates involves separation of the variables. For each normal coordinate, the equation of a pure one-dimensional harmonic oscillator is valid. In the mentioned paper by E.Schrödinger it is explicitly shown that the coordinate q_k moves predominantly in accordance with the equation (α).

However, also for non-quasi-elastic forces, quantum mechanics, at high quantum numbers, must furnish results equivalent to those of the classical theory, although it presumably is more difficult to conduct the individual proof.

bond between two atoms, an energy is created whose amount will exceed ϵ . For this, we will consider first the statistical probability of this state. This probability is (Ref.8)

$$W = \left(1 - \frac{\epsilon}{E}\right)^{3n-1}. \quad (1)$$

The expression, for large values of n , is transformed into the Boltzmann formula for substances with the specific heat k

$$W = e^{-\frac{\epsilon}{kT}}, \quad (1a)$$

on setting $\frac{E}{3n} = kT$.

On the other hand, an estimate of the average duration τ of such a state can be obtained by formulating the velocity of propagation of a perturbation in accordance with the velocity of sound v ,

$$\tau = \frac{d}{v}, \quad (2)$$

where d denotes the nearest neighbor distance of the atoms. For v , the wavelength of the most rapid vibration which has the amount of d , furnishes the following expression in accordance with $v\lambda = v$:

$$v = \nu d \quad (3)$$

whence

$$\tau = \frac{1}{\nu}. \quad (3a)$$

In combination with eqs.(1) resp. (1a), the sought time Z within which it happens once on the average that the singled-out bond has the energy ϵ will be obtained as

$$Z = \frac{1}{\nu} \left(1 - \frac{\epsilon}{E}\right)^{-3n+1}, \quad (4)$$

$$Z = \frac{1}{\nu} e^{+\frac{\epsilon}{kT}}. \quad (4a)$$

This reasoning is inaccurate in so far as it assumes that the amplitudes of neighboring atoms are mutually statistically independent. However, the following method - which avoids this assumption - leads to a predominantly similar result. /443

Let us consider a series of n atoms in which each atom, for simplicity, is assumed to have the same mass m . Let the distance of the k -th atom from the equilibrium position be x_k and let the force exerted by the k -th atom on the

(k - 1)-th atom be $\alpha(x_{k-1} - x_k)$. Then, the equations of motion will read

$$m\ddot{x}_k = \alpha(x_{k+1} - x_k) + \alpha(x_{k-1} - x_k).$$

The angular velocities ω of the natural vibrations are the solutions of the algebraic equation of the n-th degree

$$\begin{vmatrix} -m\omega^2 + \alpha & -\alpha & 0 & 0 & 0 \\ -\alpha & -m\omega^2 + \alpha & -\alpha & 0 & 0 \\ 0 & -\alpha & -m\omega^2 + 2\alpha & -\alpha & 0 \\ 0 & 0 & -\alpha & -m\omega^2 + 2\alpha & -\alpha \\ 0 & 0 & 0 & -\alpha & -m\omega^2 + \alpha \end{vmatrix} = 0. \quad (5)$$

On substituting $\frac{m\omega^2}{\alpha}$ by the new unknown y, eq.(5) will read

$$\begin{vmatrix} 1-y & -1 & 0 & 0 & 0 \\ -1 & 2-y & -1 & 0 & 0 \\ 0 & -1 & 2-y & -1 & 0 \\ 0 & 0 & -1 & 2-y & -1 \\ 0 & 0 & 0 & -1 & 1-y \end{vmatrix} = 0. \quad (5a)$$

The determinant (5a) has n rows. For low n, the solutions of eq.(5a) can be explicitly calculated; for large n, the number of solutions in various intervals can readily be given (mainly by means of the Descartes rule)*. Since all y are located between 0 and 4, the following intervals of y can be considered: 0 to 1, 1 to 2, 2 to 3, 3 to 4. The result is shown in Fig.1. It is obvious here that the eigenfrequencies are almost uniformly distributed over the entire interval. As long as the masses of the individual atoms and the interatomic forces are of the same order of magnitude, nothing will be changed on this. The case in which one bond is much weaker than the others will be discussed briefly later in the text. The distance between two neighboring atoms d, as a function of the time t, will

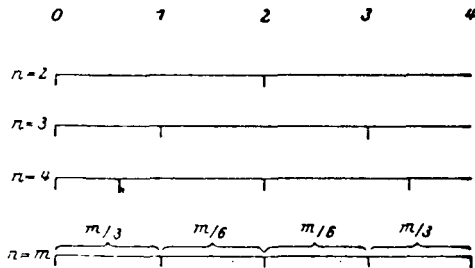


Fig.1

have the form

$$d = d_0 + x_k - x_{k-1} = d_0 + a_1 \cos \omega_1(t + \varphi_1) + a_2 \cos \omega_2(t + \varphi_2) + \dots + a_n \cos \omega_n(t + \varphi_n)$$

* For further data on the long-wave region, see P. Debye (Ref.9) as well as M. Born (Ref.10) where a further bibliography is given.

Introducing for this the angular velocity of the most rapid vibration $2\pi\nu$, we can write, with sufficient accuracy,

$$d = d_0 + c \cos \frac{2\pi\nu}{8} (t + \varphi) + c' \cos \frac{3 \cdot 2\pi\nu}{8} (t + \varphi') + c'' \cos \frac{5 \cdot 2\pi\nu}{8} (t + \varphi'') + c''' \cos \frac{7 \cdot 2\pi\nu}{8} (t + \varphi''') \quad (6)$$

in the interval $-\frac{2}{\nu} < t < \frac{2}{\nu}$. Because of the uniform distribution of the eigenfrequencies over the interval, a high value for $d - d_0$ at the time $t = 0$ will generally be produced by the fact that the coefficients c, c', c'', c''' themselves have already very high - and, specifically, approximately equal - values. In addition, the quantities φ must all be very small; in other words, the four vibrations of eq. (6) must be in phase. If the value of d is especially high, so that $\frac{\alpha(d - d_0)^2}{2} > \epsilon$, we will have, on the average,

$$\frac{\alpha(d - d_0)^2}{2} - \epsilon \sim kT.$$

Still greater discrepancies most likely will be rare. By means of eq. (6) it is easy to demonstrate that the state $\frac{\alpha(d - d_0)^2}{2} > \epsilon$ will be maintained, on the average, during a time of the order of $\frac{1}{\nu} \sqrt{\frac{2kT}{\epsilon}}$. Since its statistical probability is $\sqrt{\frac{kT}{\epsilon}} e^{-\frac{\epsilon}{kT}}$, this state will be reached $\nu e^{-\frac{\epsilon}{kT}}$ times per second.

On a more accurate mathematical interpretation of this reasoning, a value of $1 \times 15 \cdot \nu \cdot e^{-\frac{\epsilon}{kT}}$ was obtained instead of $\nu \cdot e^{-\frac{\epsilon}{kT}}$. In this case, it is assumed that the distribution of the natural vibrations has the form shown in Fig. 1 and that ϵ is large relative to kT .

According to the assumptions made, the result is valid only if the transformation proceeds by elongation along a single coordinate, i.e. (for example), by lengthening of an individual bond. If a reaction, by elongation of one atom (or radical), can take place in all three directions of space ("three-dimensional transformation"), as might specifically be the case in a multiply

bound atom, the reaction velocity will be increased by the factor $\frac{2\epsilon}{kT}$. For the case of three-dimensional transformations, this will yield the reaction velocity constant as*

* For the two-dimensional case, we have accordingly $\approx \frac{2\nu\epsilon^{1/2}}{(kT)^{1/2}} e^{-\frac{\epsilon}{kT}}$.

$$\approx \frac{2\nu\epsilon}{kT} e^{-\frac{\epsilon}{kT}}.$$

At low temperatures, not all of the vibrations are excited. Since, in this case, the most rapid vibration that is still excited, has a frequency of $\frac{kT}{h}$, this quantity will replace ν .

Until now, we have considered the case that the strength of all bonds has the same magnitude. However, it is also necessary to discuss cases in which this is not so, for example the case of an adsorbed molecule on a wall or the case of two molecules that have come into contact by collision in the gas volume. In such systems, one bond will be much weaker than all the others and will be of the order of magnitude of the cohesive forces, i.e., about ten times smaller than that of the interatomic bonds.

It is obvious that the presence of a weak bond between two vibrating polyatomic configurations permits a lower energy flux than in the case in which this same site would be strongly bound. If no forces are present, the energy flux vanishes completely.

3. Monomolecular Reactions in Gases and Solutions

We will consider here the transformation respectively the degradation of molecules that are sufficiently large to correspond, with sufficient accuracy, to eq.(4a). This means that the influx of energy to the molecule no longer is the main velocity-determining factor and that only internal processes are of any significance. This is the case whenever the molecule is sufficiently large /446 to always contain the energy ϵ , even if it is struck by such a large number of extraneous impulses that the necessary energy supply is ensured.

The velocity constant κ of such monomolecular reactions, according to eq.(4a), should be

$$\kappa = \nu e^{-\frac{Q}{RT}} \quad (7)$$

where Q denotes the heat of activation.

For three-dimensional transformations, as mentioned above, this changes to

$$\kappa = \frac{2\nu Q}{RT} e^{-\frac{Q}{RT}}.$$

The "temperature-independent factor" of monomolecular reactions is thus equal to the atomic frequency which, in the case of three-dimensional reactions, must be multiplied by $\frac{\epsilon}{kT}$. The order of magnitude of the atomic frequency is

5×10^{12} to $5 \times 10^{13} \text{ sec}^{-1}$, such that

$$\kappa = 5 \cdot 10^{12} e^{-\frac{Q}{RT}} \text{ to } 5 \cdot 10^{13} e^{-\frac{Q}{RT}}.$$

This number, however, can increase to 20 times the original value if the reaction, by displacement, can take place in several directions.

This result agrees with the practical experience that the temperature-independent factor of the reaction velocity constant in monomolecular reactions practically always has the same value, ranging in order of magnitude from 10^{13} to 10^{14} . This law was expressed already in the equation, established by S. Dushman (Ref.11),

$$\kappa = \nu^* e^{-\frac{h\nu^*}{kT}}$$

since the discrepancies between $\nu^* = \frac{Q}{Nh}$ and our ν (resp. $\frac{2\nu Q}{RT}$) are within the scattering of the test data.

A general view over the temperature-independent factors of monomolecular reactions is given in Fig.2. The graph contains the reactions in solution, compiled by J.A.Christiansen (Ref.12), as well as the values for the following 447 gas reactions: $2\text{N}_2\text{O}_5 = 2\text{N}_2\text{O}_4 + \text{O}_2$ (Ref.13, 14); decomposition of CH_3COCH_3 (Ref.15); $\text{CH}_3\text{N}_2\text{CH}_3 = \text{N}_2 + \text{C}_2\text{H}_6$ (Ref.16); decomposition of $\text{C}_3\text{H}_7\text{N}_2\text{Cl}_3\text{H}_7$ (Ref.17); $\text{CH}_3\text{OCH}_3 = \text{CH}_3 + \text{H}_2 + \text{CO}$ (Ref.18); decomposition of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (Ref.19); decomposition of $\text{CH}_3\text{CH}_2\text{CHO}$ (Ref.20); racemization of pinene (Ref.21).

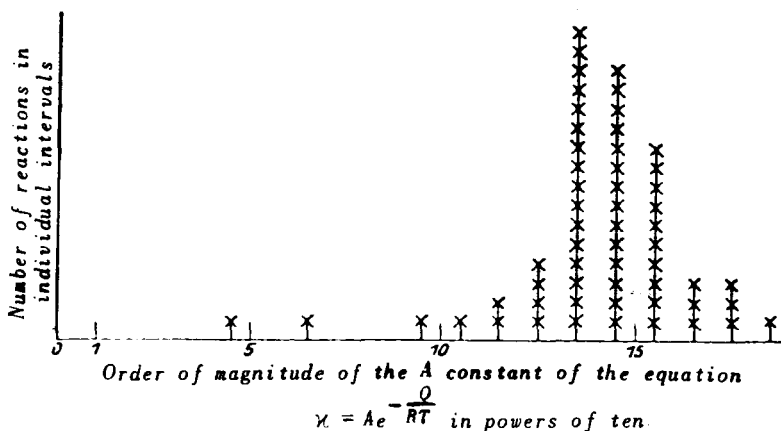


Fig.2

In part, the scattering may be due to the uncertainty of the measurement (specifically of the heat of activation), but the approximation used in our considerations may be responsible for the discrepancy.

In view of the strongly upward diverging values, it might well be that the

factors are enlarged by chain reactions. For deviations toward the bottom, if these were found to be real, further refinement of the theory might furnish an explanation.

Before discussing other applications of eq.(7), let us briefly review the reaction course in gases at low pressures. In the limiting case of low pressures, the rate of the energy inflow is decisive for the reaction velocity. If, during each collision, full energy exchange were to take place between the colliding molecules, the probability for transfer of an energy greater than /448

$\epsilon = \frac{Q}{N}$ would be

$$\frac{1}{(s-1)!} \left(\frac{\epsilon}{kT} \right)^{s-1} e^{-\frac{\epsilon}{kT}}$$

so that the reaction velocity constant κ would become (Ref.22)*

$$\kappa = S \frac{1}{(s-1)!} \left(\frac{\epsilon}{kT} \right)^{s-1} e^{-\frac{\epsilon}{kT}},$$

where S is the number of collisions.

This equation must be modified in view of the fact that the energy exchange, as mentioned in Section 2, takes place only to a limited extent because of the weak linkage formed between two colliding molecules, which finally leads to a decrease in κ .

4. Rate of Evaporation

Our concepts can also be applied to the subject of rate of evaporation. However, this case will be treated only as a typical example for our concepts, since the velocity of the process itself had been calculated earlier (Ref.29, 30)*, on the basis of equilibrium and reverse reaction. Our own approach is /449

* Based on this equation, E.Wigner (Ref.23) showed that the velocity of the monomolecular gas reactions known at that time could be explained by influx of energy via collisions. The same subject was investigated by Lewis and Smith (Ref.24). Christiansen and Hinshelwood (Ref.25, 26) further investigated and advanced this problem. The transition from the critical region of low pressures to the monomolecular course, occurring at high pressures, was studied by Rice and Ramsperger as well as by I.S.Kassel (Ref.27, 28) who used the necessity of transition of the heat of activation to a certain degree of freedom as basis. The result of their work remains unchanged by our findings.

** See also the summary presentation by Herzfeld, loc.cit., pp.229ff. The direct calculation, of the rate of evaporation, given by Herzfeld at another point of his book, cannot be considered a strict derivation because of the tacit assumptions made there.

more satisfactory only in so far as it permits a direct reading of the rate of evaporation.

Since the departure of a given atom from the crystal can take place in all three directions of space, a "three-dimensional transformation" is involved here. The probability φ for evaporation of a certain atom within the very next second, will thus be, in accordance with eq.(7a),

$$\varphi = 2\nu \frac{\lambda}{RT} e^{-\frac{\lambda}{RT}}, \quad (9)$$

where λ denotes the heat of evaporation.

This equation is confirmed by the fact that, in combination with the vapor-pressure equation (Ref.31) for high temperatures (with c denoting the concentration of the saturated vapor)

$$c = \left(\frac{2\pi m}{kT} \right)^{3/2} \nu^3 e^{-\frac{\lambda}{kT}}$$

it leads to the empirical fact that an atom (molecule), striking its condensate, will adhere there: This is proved by the fact that, if the probability for this to happen is denoted by w , we find (d = lattice constant)

$$\sqrt{\frac{1}{2\pi}} c \sqrt{\frac{kT}{m}} w = \frac{2\nu}{d^2} \frac{\lambda}{kT} e^{\frac{\lambda}{kT}},$$

from which w is calculated as

$$w = \frac{1}{\pi} \frac{\lambda}{m\nu^2 d^2} \approx 1 \quad (10)$$

as found by substituting the values of λ , m , ν .

At still lower temperatures, our picture becomes somewhat more complex since, at $kT \ll h\nu$, the accommodation coefficient is found to drop distinctly.

Also a direct application of our basic concepts leads to exactly the same result. If a molecule strikes its condensate, it must execute there at least half a vibration before it can fly off again. However, during this time it will, with great probability, have lost so much energy ($\sim kT$) that it will remain trapped. Thus, the probability w for the condensation of impinging molecules will be $w \sim 1^*$.

* See also the previously cited paper by Baule (Ref.29). One could think of treating the condensation process from the viewpoint of ordinary thermal conduction, by attempting to calculate the heat flux taking place during (cont'd)

For completeness, we should mention here that the latter reasoning applies only if the atom strikes a sensitive sphere of its condensate, i.e., a site where the potential energy is lower than the heat of evaporation. The fact that such sensitive spheres almost completely cover the surface of a given crystal is expressed in eq.(10).

5. Wall Reaction

Above, we considered the velocity of monomolecular reactions in the gas volume and in solution. It can be assumed that a molecule, reacting on a wall, must be considered from the same viewpoint since the condition of sufficient energy supply, not restricting the reaction velocity, is applicable also in this case. An estimate of the velocity of wall reactions, on this basis, can be formulated as follows:

The number N_a of molecules adsorbed on the surface ω at a concentration c in the gas volume, is obtained from the heat of absorption W if the thickness d of the effective range of the adsorption forces is assumed as 10^{-8} cm:

$$N_a = \omega c d e^{\frac{W}{RT}} = \omega \cdot 10^{-8} c e^{\frac{W}{RT}}.$$

The proportion of molecules, transformed per second, in accordance with eq.(7) will be

$$\frac{1}{N_a} \frac{dN_a}{dt} = \nu e^{-\frac{Q}{RT}},$$

where Q denotes the heat of activation in the adsorbed state. From this, it follows that

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$$\frac{dc}{dt} = c \omega d \nu e^{-\frac{Q}{RT}} \approx \omega c 10^6 e^{-\frac{Q}{RT}} e^{\frac{W}{RT}}.$$

The number N^* of the molecules striking the area W is

* (cont'd) impact and recoil. However, this method must be rejected since the heat transfer equations are valid only in regions that are large with respect to the Debye "mean free path" of thermal conduction. (In the case treated here, this is supplemented by the fact that the temperature gradient is extremely large so that, also in this respect, the assumptions of the heat transfer equations are no longer satisfied.) In fact, this mode of calculation furnishes a very small value for $1 - w$ which does not agree with practical experience since $1 - w$ (just as w itself) is of the order of magnitude of one [see also Harteck (Ref.32)].

$$N^* = \omega \sqrt{\frac{RT}{2\pi M}} c \sim 10^4 \omega c$$

($T = 600$, molecular weight = 60), whence

$$\frac{dc}{dt} \sim 100 N^* e^{-\frac{Q-W}{RT}}.$$

Accordingly, the temperature-independent factor is generally not equal to the number of molecules striking the wall but considerably greater.

The experiments by Schwab and Pietsch (Ref.33) on the decomposition of methane yielded a value of $10^{4.5} \cdot N^*$ for the temperature-independent factor. Similarly, measurements on the oxidation of tungsten by oxygen performed by Langmuir (Ref.34) as well as the still unpublished experiments by L.Marton and M.Polanyi (Ref.35) on the influence of H_2O on tungsten showed exactly the same effect; here, the temperature-independent factors were $10^{2.5} \cdot N^*$ resp. $10^3 \cdot N^*$. Thus, it seems that this phenomenon is quite general. In addition to the basic explanation given above (which, naturally, needs considerable further refinement), it must be considered also (as already mentioned by Schwab and Pietsch) that the surface may be enlarged by fissures and irregularities which (in the case of large mean free paths) would cause an increase in the adsorbed amount without changing the number of collisions with the wall.

6. Final Remarks

Within a system of atoms, held together by tight bonds, the interference of natural vibrations leads to fluctuations in the amplitude of the individual atoms, of the following type: The energy of a given atom varies on the average in the same sense during a time $\frac{1}{\nu}$. During this time, the mean variation in energy is approximately kT . The frequency with which the energy increases /452 to an amount of ϵ ($\epsilon \gg kT$) is $\sim \nu e^{-\frac{\epsilon}{kT}} \text{ sec}^{-1}$. Consequently, the atomic frequency has the significance of a cycle number of the vibration energy.

If a chemical reaction or other transformation is obtained by exceeding the critical elongation of a given atom, by traversing an energy barrier (transformation), or by lifting the atom to a higher energy level (dissociation, evaporation), the frequency of occurrence of such a process will be $\nu e^{-\frac{\epsilon}{kT}}$.

The result furnishes an explanation for the well-known fact that the temperature-independent factor of the velocity constant of monomolecular reactions has the order of magnitude of 10^{14} . Similarly, the rate of evaporation is in agreement with the empirical data. In addition, the result explains the fact that the temperature-independent factor in wall reactions frequently is larger than the number of molecules impinging on the wall.

If the system contains a weak bond (molecules in collision, molecules on the wall), the energy transfer at this point will be less than over a stable bond.

Our discussion of this topic did not have the purpose of having the velocity equations furnish strictly correct values for the equilibrium. Rather, we wanted to estimate the velocity constant for cases of practical importance.

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